论坛四十二：储氢材料论坛
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42-01

Development and application scenarios of V-based hydrogen storage materials and Mg-Ca-based hydrolysis hydrogen generation technology

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V-based hydrogen storage alloy has H2 storage density as high as ~3.9wt% and >50kg H2/m3 (system), which is promising in both mobile and stationary H2 storage devices. However, they normally release about half of the hydrogen at mild conditions due to the formation of monohydrides. In this report, the phase transformation during hydrogen uptake and release processes will be discussed. Another important issue during application of the alloy focuses on the cyclic stability, which will be investigated and analyzed in this report from various aspects as well. Additionally, promising application fields of low-pressure solid-state hydrogen storage technology is discussed.

Hydrogen generation from hydrolysis of low-cost Mg-based materials is a perfect combination of hydrogen generation, storage and transportation. The theoretical hydrogen storage densities of Mg and its hydride (MgH2) are 8.2wt% and 15.2wt% (excluding H2O), respectively. However, the main by-product Mg(OH)2 covers the surface of the materials during hydrolysis process, thus preventing the reaction from proceeding. We developed the Mg-Ca alloy hydrides hydrolysis materials, which is prone to hydrolyze. Mass transfer was enhanced to improve the conversion rate by regulating the content of Ca. By further adding additives, the pulverizing efficiency, the hydrolysis performance at low temperature and the air-stability were also improved, which greatly promoted the application opportunity of the material.

Keywords： V-based hydrogen storage alloy; Hydrogen storage densities; Cyclic stability; Hydrogen generation from hydrolysis; Mg-Ca alloy hydrides hydrolysis materials

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42-02

Development and application scenarios of V-based hydrogen storage materials and

Mg-Ca-based hydrolysis hydrogen generation technology

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V-based hydrogen storage alloy has H_2 storage density as high as ~3.9wt% and >50kg H_2/m^3 (system), which is promising in both mobile and stationary H_2 storage devices. However, they normally release about half of the hydrogen at mild conditions due to the formation of monohydrides. In this report, the phase transformation during hydrogen uptake and release processes will be discussed. Another important issue during application of the alloy focuses on the cyclic stability, which will be investigated and analyzed in this report from various aspects as well. Additionally, promising application fields of low-pressure solid-state hydrogen storage technology is discussed.

Hydrogen generation from hydrolysis of low-cost Mg-based materials is a perfect combination of hydrogen generation, storage and transportation. The theoretical hydrogen storage densities of Mg and its hydride (MgH_2) are 8.2wt% and 15.2wt% (excluding H_2O), respectively. However, the main by-product $Mg(OH)_2$ covers the surface of the materials during hydrolysis process, thus preventing the reaction from proceeding. We developed the Mg-Ca alloy hydrides hydrolysis materials, which is prone to hydrolyze. Mass transfer was enhanced to improve the conversion rate by regulating the content of Ca. By further adding additives, the pulverizing efficiency, the hydrolysis performance at low temperature and the air-stability were also improved, which greatly promoted the application opportunity of the material.

Keywords: V-based hydrogen storage alloy; Hydrogen storage densities; Cyclic stability;

Hydrogen generation from hydrolysis; Mg-Ca alloy hydrides hydrolysis materials

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42-03

Ni/MoS_2 复合材料改性 MgH_2 储氢性能研究

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MgH_2 作为一种高容量储氢材料，其实际应用仍然受到热力学和动力学方面的限制。在

这项工作中，利用 Ni/MoS_2 复合材料作为催化剂对 MgH_2 进行改性研究，显著提高了 MgH_2 的动力学性能。通过添加 10wt% Ni/MoS_2，MgH_2 的起始脱氢温度从 320℃降至 198℃左右。另外，在 300℃恒温下，它可以在 10min 内提供 6.5wt%的氢气。由 Kissinger 方法计算 Ni/MoS_2 改性的 MgH_2 的脱氢活化能为 94.2kJmol^{-1}，而单纯 MgH_2 的脱氢活化能为 150.8kJmol^{-1}。通过 XRD/TEM 和 van't Hoff 法估算热焓表明 Ni/MoS_2 的复合添加不会改变 MgH_2 的吸放氢热力学。HRTEM 研究表明，Ni/MoS_2 是 MgH_2 成核和生长的活性位点。另外，Ni/MoS_2 还有助于氢分子的解离和重组。这两个因素被认为有助于 MgH_2 的储氢性能改进。本研究为改善镁基储氢材料的储氢性能提供了一种有效的策略。

关键词：Ni/MoS_2 复合材料；催化剂；热力学；动力学

42-04

镁基储氢合金的热力学调控研究

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由于 MgH_2 具有高达 7.6 质量%的储氢容量，而且地壳中镁的丰度很高，因此 MgH_2 被广泛研究，被认为是最具潜力的固态储氢材料之一。然而，MgH_2 的高热稳定性，主要是由于较强的 Mg-H 结合能，导致其脱氢温度通常高于 300°C，这限制了其在室温附近的实际应用。

一种降低 MgH_2 热力学稳定性的常见方法是通过与不易形成氢化物的过渡金属合金化。例如，当与镍合金化形成二元 Mg_2Ni 合金时，氢化物从 MgH_2 转变为 Mg_2NiH_4，脱氢焓值也从 75 kJ/mol H_2 降至 64 kJ/mol H_2。然而，由于镁在许多合金体系中的热力学不相容性，因此通过熔融法难以制备均匀分布的 Mg 基三元合金。这一技术难题可以通过采用高压扭转方法来解决。

在本研究中，我们成功地利用高压扭转法制备了一种新型富镁三元合金 Mg_4NiPd。初步结果表明，在室温下该合金可以吸收和释放氢气，这表明我们有望设计和制备接近室温氢气存储的 Mg 基合金。这将超越已知平衡相图的界限，为开发室温储氢镁基合金提供了新的可能性。